An Evaluation of PAHs, Arsenic, and Lead Background Soil Concentrations in Vermont

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INTRODUCTION

In accordance with *Act 52 (H.269)* An *Act relating to the transportation and disposal of excavated development soils legally described as solid waste (June 5, 2015)*, this study was conducted by Vermont Agency of Natural Resources, Department of Environmental Conservation, Waste Management and Prevention Division personnel with funding and technical support provided by the U.S. Environmental Protection Agency Brownfield Program. Soil samples were collected from August through November 2015.

Surface soil samples were collected spatially throughout Vermont to determine background concentrations of polycyclic aromatic hydrocarbons (PAHs), arsenic, and lead from locations presumed to not have had a known release or land use that would have been source of these contaminants. For the purposes of this study, background is defined as the concentration of PAHs, arsenic, or lead attributed to atmospheric deposition or naturally occurring minerology. These data may be used to differentiate hazardous material releases to the environment versus background conditions and subsequent soil management.

STUDY DESIGN

The process of selecting sample locations was accomplished in the following manner:

- 1) A 100 square mile grid was overlain on the state map of Vermont;
- 2) The largest municipality in each grid was identified for sample collection;
- 3) Properties targeted for sample collection included municipal parks and greens, municipal building lawns, school lawns, and town forests.

A minimum of 1 property per grid was selected for sample collection. The study included 115 grids identified by a specific letter (A through Q) and number (1-9) combination. Grids and samples were identified A through Q from north to south and 1 through 9 west to east (Statewide Sample Location Map). Several municipalities provided more than one property for sample

collection, which were designated by subsequent lower case letters i.e., K2b. Details of property locations and attributes are provided in Tables I and II.

A total of 130 property samples and 17 duplicate samples (13%) were collected. Duplicate samples were collected for quality assurance/quality control evaluation. Samples were not collected from grids A4, C2, D2, and H6 due to a lack of municipal cooperation and absence of state lands.

Potential properties were selected by using municipal maps and aerial photography. Within each grid, if a municipal property was not available then state owned lands were selected. State owned lands included parks, forests, and fish and wildlife management areas.

Properties excluded from consideration as a background location may have had one of the following attributes:

- > Current or former industrial use;
- ➤ A state identified hazardous waste site with a surficial soil issue;
- Current or former petroleum storage;
- Recent property fire;
- Visual or olfactory evidence of contamination upon site visit or sample collection;
- > Fill material containing anthropogenic debris discovered upon sample collection.

Historical property uses were researched via available Sanborn Maps and local institutional knowledge; however, a Phase I Environmental Site Assessment was not conducted on any of the sampled property locations.

FIELD SAMPLING METHODOLOGY

Using nitrile gloves and a stainless-steel hand auger, samples were collected from an interval of 0-6 inches below any observable root zone (typically 1-2 inches below ground surface). Soils were subsequently composited into a stainless-steel bowl with a stainless-steel trowel prior to sample collection. Samples were placed into 4-ounce glass jars for PAHs and 8-ounce HDPE Nalgene containers for arsenic and lead. Sample bottles were labeled with sample number, sample location, date, time, and sampler initials. While in the field, samples were kept in a cooler on ice.

The samples were then transferred to a dedicated and secure office refrigerator for holding. Chain-of-custody forms were maintained starting with the field sampler and ending with laboratory custody. Samples were shipped on a weekly basis to the EPA Region 1 New England Laboratory in Chelmsford, MA.

Field notes, inclusive of soil characteristics, photographs and site sketch of sample location, were collected and remain on file with the Waste Management and Prevention Division.

Decontamination of field equipment was conducted by first removing any adhered soils with either a paper towel or by brush, followed by brush scrubbing with Liquinox® solution and a deionized water rinse, followed by paper towel drying.

Study design and field methods adhered to the approved EPA Quality Assurance Project Plan (QAPP) for Soil Background Study (9/2015). Standard Operating Procedures for sampling shallow soil, which are included in the QAPP, were followed.

LABORATORY METHODOLOGY

PAHs samples were analyzed by a quadrapole GC/MS operating in the Selective Ion Monitoring (SIM) mode. Extraction and analysis were based on SW-846 methods 3545A, 3630C, and 8270C.

Arsenic and Lead Preparation and analysis were based on "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Revision 2, Final Update III, Methods 3050B and 6010B," respectively. Samples were analyzed using a Perkin Elmer Dual View Inductively Coupled Plasma - Optical Emission Spectrometer.

Laboratory reports are included in the Appendices.

DATA AND EVALUATION

The VTDEC's Sites Management Section Program has reviewed the results presented by USEPA Region 1 Laboratory, and concluded that the data set is of sufficient scope and quality to establish a statewide surface soil background threshold value (BTV)¹ for: Arsenic (As), and

¹ Based upon the extensive experience of the developers in environmental statistical methods, published environmental literature, and procedures described in various EPA guidance documents, ProUCL calculates the

industrial/residential background threshold values for Lead (Pb) and Benzo(a)Pyrene TEQ for PAHs².

The data for each of the target characteristic (PAHs, lead or arsenic) was reviewed statistically. VTDEC used a software package produced by EPA, that is distributed at no cost, to ensure the public and the consulting community could reproduce our analysis of the data. With this software VTDEC was able to evaluate if the data had a normal, lognormal, gamma, parametric distribution or described through non parametric analysis. Although normal distribution is most commonly known, environmental sample data is quite often skewed and is commonly not well described by "normal distribution" statistical parameters.

For the purposes of this background study, the VTDEC has referred to numerous authors to substantiate which parameters are best suited to describe each data set. In some cases the data presented a lognormal distribution, and in other cases the distribution was best described with non-parametric analysis. For each case the overall statistical analytical approach was the same, but the conclusion may be different in response to the different data distributions.

The VTDEC utilized the same data evaluation protocol approach to each data set. Outliers were first identified with a set of well established software evaluations. This first evaluation was followed up with graphical evaluations as well as consideration of ancillary geographical information that could potentially explain the conditions. Subsequently the data was evaluated to establish the proper statistical distribution characteristics. This evaluation included establishing whether or not the data set was differentiated by urban or non-urban characteristics, which could suggest a pattern based on industrial/commercial versus domestic residential land use.

data set Upper Threshold Limit (UTLs) based upon background data sets, and point-by-point onsite observations that are compared with those limits. The UTLs are the background threshold values for the data that was analyzed. Individual site observations should be compared with these UTLs.

² **Total Equivalent Quotient** method for Polyaromatic Hydrocarbons is defined by Florida Department of Environmental Protection in their "Dose Additivity Guidance", Table 4. August 3, 2016 and previously by USEPA in Table 7, page 22 "*Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons"*. *USEPA. July 1993*.

For this study, the VTDEC's goal was to provide a consistent analysis that can be followed and reproduced easily. To that end, we chose ProUCL as our statistical evaluation software.

EPA's ProUCL version 5.0 software³ was applied to analyze each dataset for distribution (histogram and boxplot), goodness of fit, and Rosner's Outlier Test (to verify and remove outliers). After outliers were removed, each dataset was re-evaluated (histogram, boxplot and goodness of fit). The background threshold value was then evaluated for each dataset.

Outliers were omitted from the data sets by using a combination of Rosner's Outlier Test and visual inspection of the histogram and box and whisker plots. 95% confidence interval and 95% coverage were utilized in determining the background threshold value.

Each data set of analytical results (Arsenic, Lead, and TEQ PAHs) was evaluated to determine whether the data reflected a statistically significant separation, as a result of discernable land use patterns. The Density of Habitable Buildings GIS layer, located on the ANR Atlas, was used to establish areas of high population density in Vermont and were considered "urban". Areas outside of this layer were considered "rural". Each location was inspected for proximity to the "density of habitable buildings" atlas layer. Sample locations inside or within an approximate 500-foot buffer of the Density of Habitable Buildings GIS layer were considered Urban. Sample locations that were engulfed, or surrounded by the Density of Habitable Buildings GIS layer were also considered Urban. Other sample locations (not inside, engulfed, or within 500 feet of the density layer) were considered Non-Urban. A column was introduced to the spreadsheet denoting the Urban/Non-urban status for each sampling location. The two subsets, established by this visual filtering, were evaluated statistically. The data set for Arsenic did not indicate a statistically significant subset separation. The Lead and PAHs subsets however indicated that this

³ U.S. EPA's statistical ProUCL program is the same software used in USGS studies as in numerous state environmental agency studies. It is useful in evaluating site specific data distribution (normal or non-normal) and in identifying potential outliers. ProUCL is available at: www.epa.gov/osp/hstl/tsc/software.htm.

visual filtering paralleled the statistical separation of the data. Upon observation of these statistically significant separations of the subsets for the respective study parameters (Arsenic, Lead, and TEQ PAHs), it was clear that for Arsenic one statewide background threshold value would be appropriate, and that for Lead and TEQ PAHs the data is clearly different in urban and rural subsets of the state. The Sites Management Section (SMS) also analyzed the dataset to create a single Statewide BTV as well as use of the median as the BTV. Lead and PAH data did not support use of these analyses based on the varied distribution of the data.

In order to comply with the statutory requirements to create statewide or regional background concentrations and the distribution of the data, the Vermont DEC determined that use of the urban and rural datasets would best be applied to the current model of how soils are regulated and categorize the "rural" dataset as "residential" and the "urban" dataset at "commercial/industrial". These values will be used statewide and will be consistent with how all other contaminated soils in the State are currently regulated.

Duplicates were assessed for quality assurance and control by relative percent difference (RPD). There was one failure in the duplicate data, and those data were removed from further evaluation.

RESULTS AND FINDINGS

ARSENIC

The full data set was evaluated statistically using EPA's ProUCL, to establish whether or not there is validity in distinguishing "residential" from "commercial/industrial" conditions. In the case of Arsenic, the two tailed t-test analysis indicated that there is no statistically significant difference between the datasets, and that one statewide (residential and commercial/industrial) background level applies.

The sampling results and the ProUCL statistical analysis of the data indicate the data is either Gamma or Lognormal in distribution. The highest Arsenic value obtained that is not considered a statistical outlier is 17 mg/kg (=17ppm). The median is 5.4ppm. The background threshold level at 95% is either 14.27 ppm (Gamma) or 15.56 ppm (Lognormal) respectively based on distribution analysis. VTDEC has adopted 16 ppm as the statewide arsenic background threshold value.

LEAD

COMMERCIAL/INDUSTRIAL LEAD

The full data set was evaluated statistically using EPA's ProUCL software, to establish whether or not there is validity in distinguishing between the datasets. In the case of Lead, the two tailed t-test analysis indicated that there is a statistically significant separation, and that this dataset is best evaluated as two separate data sets (residential and commercial/industrial).

The sampling results and the ProUCL statistical analysis of the data indicate the data is Lognormal in distribution. The highest commercial/industrial Lead value obtained that is not considered a statistical outlier is 100 mg/kg (=100 ppm). The median is 25 ppm. The background threshold level at 95% is 111 ppm based on Lognormal distribution analysis. VTDEC has adopted 111 ppm as the commercial/industrial statewide soil lead background threshold value.

RESIDENTIAL LEAD

The sampling results and the ProUCL statistical analysis of the residential data indicate the data is either Gamma or Lognormal in distribution. The highest Residential Lead value obtained that is not considered a statistical outlier is 37 mg/kg (=37 ppm). The median is 14 ppm. The background threshold level at 95% is either 36.75 ppm (Gamma) or 41.02 ppm (Lognormal) respectively based on distribution analysis. VTDEC has adopted 41 ppm as the residential statewide soil lead background threshold value.

TEQ PAHs

PAHs were evaluated as a Total Equivalency Quotient (TEQ) using the World Health Organizations (WHO) 2005 TEF (toxicity equivalence factor) values. Non detect values were included as ½ the

detection limit of the laboratory instrument. This is due to the definition of the TEQ PAHs value, and is not the result of statistical evaluation.

The full data set was evaluated statistically using EPA's ProUCL software, to establish whether or not there is validity in distinguishing the two datasets. In the case of TEQ PAHs, the two tailed t-test analysis indicated that there is a statistically significant separation and that the dataset should be evaluated as two distinct data sets.

COMMERCIAL/INDUSTRIAL TEQ PAHS

The sampling results and the statistical analysis of the data indicate the data is Lognormal in Distribution. The highest Urban TEQ PAHs value obtained, that is not considered a statistical outlier is 425.7µg/kg (=425.7ppb). The median is 93.83 ppb. The background threshold level at 95% is 579.6 ppb based on Lognormal distribution analysis. VTDEC has adopted 580 ppb as the Commercial/Industrial TEQ PAHs background threshold value.

RESIDENTIAL TEQ PAHs

The sampling results and the statistical analysis of the data indicate the data does not follow a discrete distribution. The highest residential TEQ PAHs value obtained not considered a statistical outlier is $26.18 \, \mu g/kg$ (= $26.18 \, ppb$). The median is $8.81 \, ppb$. The background threshold level at 95% is $26.18 \, ppb$ based on Non-parametric distribution analysis. **VTDEC has adopted 26 ppb as the Residential TEQ PAHs background threshold value.**

SUMMARY TABLE4

	Background Threshold Value		
Arsenic - Statewide	16	mg/kg	
Lead – Commercial/Industrial	111	mg/kg	
Lead – Residential	41	mg/kg	
TEQ PAHs - Commercial/Industrial	580	μg/kg	
TEQ PAHs – Residential	26	μg/kg	

REGIONAL EVALUATIONS OF DATA

The separate data sets for arsenic, lead, and PAHs were visually reviewed to discern any groupings related to the six physiographic regions of the State (Map 3). Those regions include the Vermont Lowlands, Green Mountains, Taconic Mountains, Valley of Vermont, Vermont Piedmont, and Northeast Highlands. No discernable visual trends were identified for either the PAHs or lead data sets. The following concentration groupings were observed for the arsenic data set. This information in addition to the statistical analysis of arsenic discussed herein supports the conclusion that the concentrations of arsenic observed state wide are dependent on geology and are not related to atmospheric deposition resultant from anthropogenic activities.

Physiographic Region	Arsenic Concentration Range (mg/kg)
Lowlands	Less than 10
Green Mountains	Less than 5
Taconic Mountains	Less than 20
Valley of Vermont	Less than 10
Vermont Piedmont	Less than 31
Northeast Highlands	Less than 10

DEVIATIONS FROM QAPP:

- 1. One field book was lost by the field crew. This affects a number of sample locations, as the field book was shared with previous sampling teams. Two other field books remain.
 - a. It is not possible to see the field notes for certain sample locations.
- 2. Some municipalities offered sampling locations. These locations were not identified by the sampling team, and may not have reflected the original selection criteria.

⁴ Quality Assurance was evaluated by calculating the relative percent difference (RPD) between parent and duplicate samples (Table III). An RPD of 50% or greater was considered unacceptable. As such, sample F1 was not included in the calculation of As-BTV.

- a. Subsequently some of the accepted sampling locations from this subset, reflected some of the highest "outlier" concentrations. Example is K2b, which had an outlier concentration of TEQ PAHs.
 - This location appears to be in the flood plain, a few hundred feet downstream of a known past manufactured gas plant, located on the river hank
 - ii. It is reasonable to exclude outliers with suspected or known anthropogenic sources of the subject compounds.
- b. The statistical analysis of the data was able to discern which data were outliers, however some anthropogenically disturbed sites may be part of the data set.
- c. VTDEC did not conduct a Phase I ESA of each proposed sampling location and cannot assert if any location in particular had verifiable recognized environmental conditions.
- d. The deviation of accepting sampling locations suggested by other parties may have contributed location sites with anthropogenic activity. This may bias the data higher.
- 3. Several sample locations are misaligned with their intended grid cell designation.
 - a. Several K5 subsamples are located within grid cell K6. These locations were incorporated at the behest of the municipality after the establishment of the protocol.
 - b. Sample N2 was sampled in grid cell M2, and thus it is mislabeled. Since the municipality in grid cell N2 did not grant us property access, we sampled from state owned land. In this case, the sample location was Emerald Lake State Park, which is located within both grid cells M2 and N2. Consequently, no sample was taken in grid cell N2.

Although there were deviations from the QAPP the VTDEC does not believe that any of these deviations impacted the validity of the data or our ability to determine background threshold values for Arsenic, Lead and PAHs in Vermont.